RADIATION EXPOSURES IN THE FLORIDA PHOSPHATE INDUSTRY

W.A. Mills, R.J. Guimond, and S.T. Windham
Office of Radiation Programs
U.S. Environmental Protection Agency
Washington, D.C. 20460

1. INTRODUCTION

Studies of natural uranium and thorium in phosphate ores produced in the United States indicate that concentrations of these natural materials range from about 10 to 400 ppm and 2 to 20 ppm, respectively (1,2). In the rich marine phosphite deposits of Florida, uranium is present in concentrations in the range 100-150 ppm. Uranium daughters in the phosphate ores, at least through radium-226, are usually in secular equilibrium.

The purpose of present studies of this industry by the U.S. Environmental Protection Agency is to assess the radiological impact of phosphate mining, processing, use, and related activities. The study includes an evaluation of the effectiveness of controls and, in areas where controls appear to be insufficient, the development of appropriate standards and guides. This paper summarizes findings to date.

2. OVERVIEW OF THE INDUSTRY'S OPERATIONS

In 1974, the total U.S. production of marketable phosphate rock was about 46 million tons with approximately 80 percent coming from the Florida phosphate industry (3). Consequently, the large scale operations of this industry in one regional area may lead to several types of impact on the environment. At present, the domestic marketable phosphate rock production accounts for about 40 percent of the total world production.

The standard mining practice in Florida is to strip the overburden and mine the phosphate matrix. Approximately 5000 acres of land are mined per year in Florida. At the beneficiation plant, the matrix is processed to upgrade its P_2O_5 concentration. The output materials from this operation are marketable phosphate rock, sand tailings and slimes. These materials are produced in a 1:1:1 ratio. Table 1 lists the uranium, thorium, and radium-226 activities for these materials.

TABLE 1: Natural Radioactivity Concentrations in Florida Phosphate Mine Products and Wastes (pCi/gm)

Material	Ra-226	U-238	Th-230	Th-232
Marketable Rock	42	41	42.3	0.44
Slimes	45	44	48	1.4
Sand Tailings	7.5	5.3	4.2	.89

Mined-out areas are used for the disposal of sand tailings and slimes, in addition to overburden. Several Florida slime ponds have discharges to the environment. Since most of the radioactivity in the beneficiation wastes is present in the slimes, the concentration of radium-226 was determined for slime. The concentration of dissolved radium-226 was less than 5 pCi/liter at all facilities. The undissolved radium-226 concentration ranged from 10 to 2000 pCi/liter and was highly dependent on the total suspended solids in

10903593

the slimes. Although no chemical process is used to treat the discharge from the slime ponds, concentrations of radium-226 in effluents were all less than 3 pCi/liter. The reduction of total radium-226 from the raw slime to the effluent ranged from 92 percent to greater than 99.9 percent. This was primarily due to the removal of suspended solids by settling.

Marketable phosphate rock from Florida is processed into two major products, fertilizers in "wet process" phosphoric acid plants and elemental phosphorus in electric furnace plants. In the "wet process" phosphoric acid plant, phosphate rock is mixed with 93 percent sulfuric acid. This reaction produces phosphoric acid and gypsum. Following the reaction in the attack vessel, the mixture is filtered and the separated gypsum is pumped to a large pile where it is allowed to dewater. Since approximately 4 metric tons of gypsum are produced per ton of phosphoric acid, a large phosphoric acid plant would produce about 2.5 million metric tons of gypsum per year (4). Approximately one percent of the radium-226, 60 to 80 percent of the thorium-230, and 80 percent of the uranium in phosphate rock are dissolved by this acid process.

Table 2 lists the average radioactivity concentrations for the fertilizer products and phosphogypsum by-product of several wet-process type facilities in Florida. Phosphoric acid samples were found to contain from 50,000 to 100,000 pCi/liter uranium-238 and less than one pCi/liter radium-226. The concentration of uranium appears to vary directly with the concentration of P_2O_5.

TABLE 2: Natural Radioactivity Concentrations in Materials Produced from Florida Phosphates (pCi/gram)

Material	Ra-226	U-238	Th-230	Th-232
Normal Superphosphate	21.3	20.1	18.0	0.6
Diammonium Phosphates	5.6	63	65	0.4
Concentrated Superphosphate	21	58	48	1.3
Monoammonium Phosphates	5	55	50	1.7
Phosphoric Acid*	<1	25.3	28.3	3.1
Gypsum	33	6	13	0.3

*29 percent acid.

Each "wet process" phosphoric acid plant incorporates a large cooling pond (∿500 acres) of contaminated water for recycle in the facility. During periods of excess rainfall it becomes necessary to discharge water from these ponds to nearby streams. Raw process water was found to contain approximately 50 to 90 pCi total radium-226 per liter and approximately 400 to 2000 pCi/liter of uranium-238. To prepare process water for discharge to the environment, the pH must be increased from 1.5-2.0 to 6-9. To accomplish this, slaked lime is normally added. Our studies have shown that this treatment is highly effective in removing radionuclides from the effluent. Radium-226 reductions of greater than 96 percent were observed, with similar reductions in uranium and thorium. As a result of the effectiveness of this treatment, the Agency's permits for phosphoric acid plants usually stipulate an acceptable pH range of 6-9 for treated effluent which ensures minimization of radioactivity discharges.

In the thermal (electric furnace) processing of phosphate rock, silica and coke are added; this mixture is reduced to form elemental phosphorus. Ferrophosphorus and calcium silicate slag by-products are also formed in the process. Most of the uranium and radium-226 activities in the input phosphate rock are transferred to slag.

3. RECLAIMED LAND USE

Approximately 100,000 acres of land have been mined for phosphate rock in Florida. To date, about 25,000 acres of the mined lands have been reclaimed for residential and commercial development, farming, and grazing (5). It is estimated that about 1000 structures have been built on these lands. Since reclaimed lands are composed of overburden, leach zone material, matrix, sand tailings, and/or slimes, they frequently contain radium-226 concentrations substantially higher than the 0.1 to 3 pCi/gram typical of U.S. soils. Concentrations up to 98 pCi/gram have been measured in these reclaimed soils. However, radium-226 concentrations in the reclaimed land soils generally range between 10 to 30 pCi/gram to depths greater than 20 feet. A considerable quantity of radon-222 is produced. This radon-222 diffuses to the ground surface and through the foundations of structures leading to build-up of short-lived radon daughters. Average indoor radon daughter levels over a one-year period were obtained for several structures selected at random on reclaimed land and on land distant from the phosphate region. These data are summarized in Table 3.

TABLE 3: Percentage Range of Radon Daughter Levels

Reclaimed Land (n=13)		Nonreclaimed Land (n=9)	
0.05 to 0.1 WL	: 38%	0.05 WL	: -0-
0.01 to 0.05 WL	: 31%	0.01 to 0.05 WL	: 22%
0 to 0.01 WL	: 31%	0 to 0.01 WL	: 78%

We believe that the potential excess lung cancer risk associated with the higher levels, warrant additional studies to define the scope and magnitude of this problem. Based on the assumption that excess lung cancers will double per 60 CWLM exposure, we can associate the highest annual average working level observed, of 0.1 WL for continuous occupancy and an average lifetime (70+ years), with a 6 to 10 times increase in lung cancer. The estimate of the doubling dose is based on the excess cancer observed in uranium miners. If, as seems likely now, the doubling dose is lower for a general population, the estimated health risk would be proportionately greater, possibly by as much as a factor of 2.

4. PRINCIPAL EXPOSURE PATHWAYS

There are numerous pathways which could cause exposure to the public due to operation of the Florida phosphate industry. These include exposures resulting from effluents, emissions, ground waters, using the industry's products and by-products, living and working on reclaimed land, and working in the industry. The normal effluents from phosphate mine slime ponds and phosphoric acid plants are readily controllable to limit total radium-226 discharges to surface waters to less than 3 to 4 pCi/liter. It is highly unlikely that such discharges would result in excess radium-226 concentrations greater than 0.5 pCi/liter downstream. However, accidental failure of slime pond dikes could significantly increase the radium-226 concentrations at user points.

Many shallow well water supplies in Central Florida contain radium-226 concentrations greater than the limit of 5 pCi/liter radium-226 and radium-228 contained in EPA's Safe Drinking Water Regulations. However, it is uncertain to what extent the levels are due to the natural presence of uranium in phosphate ores or to operations of the industry.

Data collection and evaluation of air emissions from elemental phosphorus and phosphoric acid plants are incomplete. However, there are some preliminary indications that significant quantities of Po-210 may be emitted from these facilities due to volatization during calcining or furnace operations.

Workers in the phosphate operations come in close contact with large amounts of phosphate ores, products, and wastes along with inhalation of dust generated by unloading, crushing, drying, and other activities. The highest potential exposures were observed in areas of high dust concentrations in and around the phosphoric reactor vessel. It has been estimated that direct gamma dose equivalents for workers range from 30 to 300 mrem/yr (6). The maximum potential dose equivalent rate to the lungs is about 5 rem/yr. However, using corrections for occupancy this dose equivalent rate is reduced by at least a factor of ten. We do not believe workers in the phosphate industry are being exposed at levels greater than radiation protection guides for the general population. However, we do see a need for more prudent "good housekeeping" measures, particularly with respect to dust levels in various operations.

Population exposures to the indoor radon daughters in structures appear to be the most significant public health problem, and efforts are being made to develop radiation protection guidelines to control exposures to this source. As an interim measure we have provided the State of Florida a screening level which allows continued land development without a significant health impact. This interim guideline is based on a gamma exposure of less than 10 μR/hr (including background) which can be associated with a guesstimate of a radon daughter level less than 0.01 WL.

Other aspects of the industry which require further study include the impact of using by-product slag and gypsum for construction materials, the uptake of radionuclides by crops due to fertilizer use or growing on reclaimed lands, evaluating control technologies to limit indoor radon daughter levels, and assessing the impact of recovering uranium fuel from phosphate materials. Efforts are being made to complete scoping of the radiological impact of this industry and to controlling this impact when necessary.

REFERENCES

(1) MENZEL, R.G. "Uranium, Radium, and Thorium Control in Phosphate Rocks and their Possible Radiation Hazard," J. Agr. Food Chem., Vol. 16, No. 2, pp 231-234 (1968).

(2) GUIMOND, R.J., WINDHAM, S.T. "Radioactivity Distribution in Phosphate Products, By-Products, Effluents, and Wastes, ORP/CSD-75-3, USEPA, Washington, D.C. (August 1975).

(3) STOWASSER, W.F. "Phosphate Rock," 1974 Bureau of Mines Mineral Yearbook, preprint, USDoI, Washington, D.C. (1976).

(4) SLACK, A.V., ed. "Disposal or Use of Gypsum," Phosphoric Acid, Vol. 1, Part III (1968).

(5) OFFICE OF RADIATION PROGRAMS: "Preliminary Findings - Radon Daughter Levels in Structures Constructed on Reclaimed Florida Phosphate Land," Technical Note ORP/CSD-75-4, USEPA (September 1975).

(6) WINDHAM, S.T., PARTRIDGE, J., HORTON, T. "Radiation Dose Estimates to Phosphate Industry Personnel," EPA-520/5-76-014, USEPA, Montgomery, Alabama (1976).